PMR Polyimide Composites for Aerospace Applications

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PMR POLYIMIDE COMPOSITES FOR AEROSPACE APPLICATIONS

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ABSTRACT

Fiber reinforced PMR polyimides are finding increased acceptance as engineering materials for high performance structural applications. Prepreg materials based on this novel class of highly processable, high temperature resistant polyimides, which were first developed at the NASA Lewis Research Center, are commercially available and the PMR concept has been incorporated in several industrial applications. This paper reviews the current status of PMR polyimides. Emphasis is given to the chemistry, processing, and applications of the first generation PMR polyimide known as PMR-15.

INTRODUCTION

Advanced fiber reinforced polymer matrix composites are achieving acceptance as engineering materials for the design and fabrication of high performance aerospace structural components. Epoxy resins are the most widely used polymer matrix materials because of their excellent mechanical properties and processing characteristics. In fact, the processing characteristics of epoxies have been adopted as "practical standards" for measuring the processability of other potential matrix resins. A disadvantage of epoxy resins is that their upper-use temperature is limited to approximately 175° C. Until recently, the intractable nature of higher temperature resistant polymers, which in theory could provide nearly a two-fold increase in use-temperature, has prevented the realization of the full potential of these polymers as matrix resins for high temperature polymer matrix composites.

In response to the need for high temperature polymers with improved processability, investigators at the NASA Lewis Research Center developed the novel class of addition-type polyimides known as PMR (for in situ polymerization of monomer reactants) polyimides. 1-3 The PMR concept consists of impregnating the reinforcing fibers with a monomer mixture dissolved in a low boiling point alkyl alcohol. The monomers are essentially unreactive at room temperature, but undergo sequential in situ condensation and ring-opening addition crosslinking reactions at elevated temperatures to form a thermo-oxidatively stable polyimide matrix resin. Because the final in situ reaction occurs without the release of volatile materials, high quality void-free composites can be fabricated by either compression or autoclave molding techniques. Thus, the highly processable PMR polyimides have made it possible to realize much of the potential of high temperature resistant polymers.

Our research has identified monomer reactant combinations for several PMR polyimides differing in chemical composition. The earliest, or "first generation", PMR matrix is designated PMR-15. Prepreg materials employing PMR-15 are commercially available from the major suppliers of composite materials.

The purpose of this paper is to review the current status of PMR polyimides. Emphasis is given to reviewing the aerospace applications of PMR-15 polyimide composites.

DISCUSSION

PMR Polyimide Chemistry

Condensation-type aryl polyimides are generally prepared by reacting aromatic diamines with aromatic diamhydrides, with aromatic tetracarboxylic acids, or with dialkyl esters of aromatic tetracarboxylic acids. The diamine-diamhydride reaction is pre-

ferred for preparing films and coatings, whereas the latter two combinations of reactants are generally employed for the preparation of matrix resins. Prepeg solutions are prepared by dissolving the appropriate reactants in high boiling point aprotic solvents (e.g., N-methyl-2-pyrollidone, NMP) or in solvent mixtures containing an aprotic solvent. During composites fabrication, volatilization of the solvent and the condensation reaction byproducts results in high void content composites having inferior mechanical properties and thermo-oxidative stability.

Figure 1 outlines some salient features of the PMR polyimide approach for the fabrication of composites. In the PMR approach, the reinforcing fibers are hot-melt or solution impregnated with a monomer reactant mixture dissolved in a low-boiling-point alkyl alcohol, such as methanol or ethanol. The monomer reactant mixture contains a dialkyl ester of an aromatic tetracarboxylic acid, an aromatic diamine, and a monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid (NE). The number of moles of each reactant is governed by the following ratio:

n:(n+1):2

Where n, (n + 1), and 2 are the number of moles of the dialkyl ester of the aromatic tetracarboxylic acid, the aromatic diamine, and NE, respectively. In situ polymerization of the monomer reactants (PMR) occurs when the impregnated fibers are heated. A condensation reaction forming low molecular weight norbornenylendcapped oligomers occurs in the temperature range of 121°-232° C. At temperature in the range of 275°-350° C, the norbornenyl groups undergo a ring-opening reaction generating maleic end-groups and cyclopentadiene. The maleic functions immediately copolymerize with the cyclopentadiene and unreacted norbornenyl groups to form a crosslinked polyimide without the evolution of volatile materials.

In the initial study which established the feasilibity of the PMR concept, it was noted that a PMR matrix prepared from a monomer mixture consisting of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), 4,4'-methylene-dianiline (MDA), and NE exhibited a higher level of thermo-oxidative stability at 316° C than a PMR matrix made from the dimethyl ester of pyromellitic acid, MDA and NE. This unexpected finding was confirmed in a subsequent study and the number of moles of BTDE which provided the best overall balance of processability and 316° C thermo-oxidative stability was found to be 2.087, corresponding to a PMR polyimide having a formulated molecular weight (FMW) of 1500. PMR matrices employing BTDE are referred to as "first generation" materials. Also, the stoichiometry of a PMR resin is generally denoted by dividing the FMW by 100. Thus, the first generation PMR matrix prepared from BTDE,

MDA, and NE having an FMW of 1500 is widely known as PMR-15. Prepreg materials based on PMR-15 are commercially available from the major prepreg suppliers. The structures of monomers used in PMR-15 are shown in Table I.

The early investigations 1,4 also clearly demonstrated the efficacy and versatility of the PMR approach. By simply varying the chemical nature of the either the dialkyl ester acid or aromatic diamine, or both, and the monomer reactant stoichiometry, PMR matrices having a broad range of processing characterisitics and properties were prepared. A modified PMR-15, called LARC-160, has been prepared by substituting an aromatic polyamine for MDA.5 Other studies 6 have shown that the PMR approach has excellent potential for "tailor making" polyimide matrix resins with specific properties. For example, as shown in Figure 2, the resin flow characteristics (amount of resins exuded during processing) can be varied, or "tailored", over a broad range by simple adjustment of FMW (monomer stoichiometry). However, as shown in Figure 3, the higher-flow formulations exhibited decreased thermo-oxidative stability at 288° C. The reduction in resin flow and increase in thermo-oxidative stability at 288° C with increasing FMW clearly show the sensitivity of these properties to imide ring or alicyclic contents. The reduction in resin flow with increased FMW (increased imide ring content) also serves to qualitatively account for the intractable nature of linear condensation polyimides at an early stage in their process history.

Partial or complete replacement of BTDE with the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE) significantly improved the thermo-oxidative stability of "first generation" PMR resins.^{7,8} The HFDE-PMR compositions are referred to as "second generation" materials to distinquish them from the "first generation" BTDE-PMR materials. The "second generation" HFDE-PMR resins have not been accepted as matrix resins because of the lack of a commercial source for the anhydride of HFDE.

As mentioned earlier, current technology PMR-15 polyimide prepreg solutions are generally prepared by dissolving the monomer
mixture in a low-boiling-point alkyl alcohol. Although the
volatility of these solvents is highly desirable for obtaining
void free composites, it does limit the tack and drape retention
characteristics of unprotected prepreg exposed to the ambient.
PMR-15 monomer reactants and a mixed solvent have been identified
which provide prepreg materials with improved tack and drape retention characteristics without changing the basic cure chemistry,
processability, or thermo-oxidative stability. The modifications consist of substituting higher alkyl esters for the methyl
esters in NE and BTDE and using a solvent mixture (3:1 methanol/
1-propanol) in lieu of pure methanol.

Composites Processing and Properties

High pressure (compression) and low pressure (autoclave) molding cycles have been developed for fabrication of fiber reinforced PMR composites. Although the thermally-induced addition-cure reaction of the norbornenyl group occurs at temperatures in the range of 275° to 350° C, nearly all of the processes developed use a maximum cure temperature of 316° C. Cure times of 1 to 2 hours followed by a free standing post-cure in air at 316° C for 4 to 16 hours are also normally employed. Compression molding cycles generally employ high rates of heating (5 to 10° C/min) and pressure in the range of 3.45 x 10^6 to 6.0 x 10^6 N/m². Vacuum bag autoclave processes at low heating rates (2 to 4° C/min) and pressures of 1.38 \times 10⁶N/m² or less have been successfully used to fabricate void-free composites. The successful application of autoclave processing methodology to PMR polyimides results from the presence of a thermal transition, termed "melt-flow", which occurs over a fairly broad temperature range. 10 The lower limit of the melt-flow temperature range depends on a number of factors including the chemical nature and stoichiometry of the monomer reactant mixture, and the prior thermal history of the PMR prepreg. Differential scanning calorimetry studies have shown the presence of four thermal transitions which occur during the overall cure of a PMR polyimides. 11 The first, second and third transitions are endothermic and are related to the following: (1) melting of the monomer reactant mixture below 100° C, (2) in situ reaction of the monomers at 140° C, and (3) melting of the norbornenyl terminated prepolymers at the range of 175° to 250° C, referred to as the melt-flow temperature range. The fourth transition, centered near 340° C, is exothermic and is related to the addition crosslinking reaction. To a large extent the excellent processing characteristics of PMR polyimides can be attributed to the presence of these widely separated and chemically distinct thermal transitions.

The recommended final cure temperature of 316° C for PMR-15 exceeds the temperature capabilities of many industrial autoclave facilities which were originally acquired for processing of epoxy matrix composites. Recent studies have shown that a significant reduction in cure temperature of PMR-15 can be achieved by replacing 50 mole percent of the NE with p-aminostyrene. Cure studies of the mixed endcap system showed that the final cure temperature of PMR-15 could be reduced to 260° C without sacrificing its 316° C thermo-oxidative stability.

Many studies have been conducted to determine the effects of various hostile environments on the physical and mechanical properties of PMR-15 composites. Glass, ¹³ graphite, ¹⁴⁻¹⁶ and Kevlar¹⁷ PMR-15 composites have been investigated. Figure 4 shows the excellent 316° C interlaminar shear strength retention characteristics of PMR-15 composites made with four different

graphite fibers. 15 The difference in strength levels between the Celanese Celion 6000 composites and the three other composites was attributed to differences in fiber surface morphologies.

In the study 18 to correlate the stability of the individual resin components in PMR-15 with the weight loss of Celion 6000/PMR-15 composites during 2200 hours of exposure in air at 316°C, the stability of the resin components increased in the following order:

MDA < NE << BTDE

After 1200 to 1500 hours of exposure, the NE crosslinker exhibited a marked increase in degradation which correlates with the 316° C performance of PMR-15 composites. Excellent retention of composite mechanical properties and low composite weight loss are generally observed for 316° C exposure in air up to about 1500 hours. Thus, it would appear that the 316° C thermo-oxidative stability of the nobornenyl crosslinker determines the useful lifetime of PMR-15 composites at 316° C. However, in a recent study it was found that the addition of low levels (4 and 9 mole percent) of a monofunctional norbornenyl crosslinker to PMR-15 increased the composite thermo-oxidative stability and resin flow during compostie processing. 19 Although the modified PMR-15 composites exhibited lower initial properties at 316° C than unmodified PMR-15 composites, the addition of small quantities of a monofunctional norbornenyl crosslinker to PMR-15 to increase the 316° C thermooxidative stability appears to be a promising approach. At the present time, however, the composition of PMR-15 remains unchanged from the original composition developed in the early seventies.

Aerospace Applications of PMR-15 Polyimide Composites

One of the most rewarding aspects of the PMR polyimide development has been the successful demonstration of PMR-15 polyimide composite materials as viable engineering materials. Prepregs, molding compounds and even adhesives based on PMR-15 have been commercially available from the major suppliers of composite materials since the mid seventies. Because of their commercial availability, processability, and excellent retention of properties at elevated temperature, PMR-15 composites have been used to fabricate a variety of structural components. These components range from small compression molded bearings to large autoclave molded aircraft engine cowls and ducts. Processing technology and baseline materials data are being developed for the application of PMR-15 composites in aircraft engines and nacelles, space structures, and weapon systems. Some representative applications of PMR-15 composites are listed in Table II. None of the components listed in the table, except the ion engine beam shield, are applications in the sense that the components are currently being

produced. However, several of the components listed in Table II are scheduled for production introduction in the near future. A brief discussion of each of the components listed in Table II follows.

The blade illustrated in Figure 5 was the first structural component fabricated with a PMR-15 composite material. The reinforcement is HTS graphite fiber. The blade design was conceived by Pratt and Whitney Aircraft (PWA) for an ultra-high-speed fan stage. 20 Blade tooling and fabrication were performed by TRW Equipment. 21 The blade span is 28 cm and the chord is 20 cm. The blade thickness ranges from about 1.3 cm just above the midpoint of the wedge shaped root to 0.06 cm at the leading edge. At its thickest section the composites structure consists of 77 plies of material arranged in varying fiber orientation. The "line of demarkation" visible in Figure 5 at approximately one-third the blade-span from the blade-tip resulted from a required change in fiber orientation from 40 degrees in the lower region to 75 degrees in the upper region to meet torsional stiffness requirements. Ultrasonic and radiographic examination of the compression molded blades indicated that they were defect free. Although some minor internal defects were induced in the blade during low cycle and high cycle fatique testing, the successful fabrication of these highly complex blades established the credibility of PMR-15 as a processable matrix resin.

Figure 6 shows the inner cowl installed on an experimental engine, called QCSEE for a Quiet Clean Short-Haul Expermiental Engine, developed by General Electric (GE) under contract with NASA Lewis. 22 The cowl defines the inner boundary of the fan air flowpath from the fan frame to the engine core nozzle. cowl was autoclave fabricated by GE from PMR-15 and Union Carbide's T300 graphite fabric. The cowl has a maximum diameter of about 91 cm and is primarily of honeycomb sandwich construction. Hexcel's HRH327 fiberglass polyimide honeycomb was used as the core material. The honeycomb core was bonded to the inner surface of the premolded outer skin with duPont's NR150B2G adhesive. The inner skin was then co-cured and bonded with NR150B2G to the core surface of the honeycomb core/outer skin assembly. Complete details about the cowl fabrication process are given in reference 23. The cowl was installed on the QCSEE engine and did not exhibit any degradation after more than 300 hours of ground engine testing. The maximum temperature experience by the cowl during testing was 260° C. 24 The successful autoclave fabrication and ground engine test results of the QCSEE inner cowl established the feasibility of using PMR-15 composite materials for large engine static structures.

Under a jointly sponsored Wavy/NASA Lewis program (NAS3-21854), GE is developing a T300 Graphite fabric/PMR-15 composite outer duct to replace the titanium duct presently used on the F404 engine for the Navy's F18 strike fighter. The titanium duct is a sophis-

ticated part made by forming and machining titanium plates followed by chem milling to reduce weight. A preliminary cost-benefit study indicated that significant cost and weight saving 25 could be achieved by replacing the titanium duct with a composite duct. The F404 composite outer duct differs from the QCSEE inner cowl in several important respects. The F404 duct is a monolithic composite structure, needs to withstand fairly high loads and, perhaps most importantly, the F404 duct is to be a production component and not a "one-of-a-kind" demonstration component. A full-scale composite duct (97 cm diameter by 165 cm length by 0.2 cm wall thickness) has been autoclave fabricated. The overall duct fabrication process consists of many operations. The sequence of the major operations is as follows: (1) autoclave fabrication of the composite shell, (2) ultrasonic inspecton, (3) adhesive bonding of T300 fabric/PMR-15 ply buildups to the shell using PMR-15 as the adhesive, (4) drilling of the buildups and cutting of the shell into two halves and (5) attachment of the split line stiffeners and titanium end-flanges. Figure 7 shows a photograph of the completed outer duct. The duct was installed on an F404 engine (Figure 8) and has successfully undergone nearly 900 hours of engine testing. The T300/PMR-15 composite outer duct is tentatively scheduled for production introduction in 1985.

Figure 9 shows a full-scale composite forward inner duct fabricated by GE for their F101 DFE (Derivative Fighter Engine). The approximate dimensions of the duct which was autoclave fabricated from T300 graphite fabric/PMR-15 are 102 cm diameter by 38 cm length by 0.15 cm wall thickness. Engine testing demonstrated that the composite duct was fully functional and met engine performance requirements. The T300/PMR-15 composite inner duct is currently scheduled for production introduction in 1985.

The current bill-of-materials inlet particle separator swirl frame on GE's T700 engine is an all metal part that involves machining, shape-forming, welding, and brazing operations. Design studies conducted under U. S. Army contract number DDAK51-79-C0013 indicated that the fabrication of a metal/composite swirl frame could result in a cost and weight savings of about 30 percent. Figure 10 shows a schematic diagram of a section of the metal/composite swirl frame that was fabricated from 410 stainless steel and various kinds of PMR-15 composite materials. The outer casing uses stainless steel in the flow path area to meet anti-icing temperature requirements and T300 and glass fabric/PMR-15 hybrid composite to meet structural requirements. The T300/glass hybrid composite was selected on the basis of both cost and structural considerations. An aluminum-coated glass fabric/PMR-15 composite material is utilized in the inner hub flowpath to meet heat transfer requirements for anti-icing. The glass fabric/PMR-15 composite utilized for the front-edge and front-inner surfaces was selected because of cost as well as temperature considerations. A fullscale (0.D. ä 51 cm) metal/composite swirl frame has been subjected to sand erosion and ice ball impact tests. The metal/composite swirl frame provided improved particle separation and successfully met the impact test requirements. Fabrication feasibility has been demonstrated and if the metal/composite swirl frame successfully meets all of the performance rquirements, the metal/composites T700 swirl frame is scheduled for engine testing in 1985.

Figure 11 shows a photograph of a DC-9 aircraft. The inserts schematically depict the design of the presently used metal reverser stang fairing and a composite redesigned fairing developed by Douglas Aircraft Company under the NASA Lewis Engine Component Improvement Program. Studies had shown that a redesigned fairing provided an opportunity to reduce baseline drag and would result in reduced fuel consumption. The fairing serves as the aft enclosure for the thrust reverser actuator system on the nacelle of the JT8D engine and is subjected to a maximum exhaust temperature of 260° C during thrust reversal. A Kevlar fabric/PMR-15 composite fairing has been autoclave fabricated and flight-tested. Compared to the metal components, the composite fairing resulted in a one percent airplane drag reduction (1/2 percent had been anticipated) and a 40 percent reduction in component weight.

Figure 12 is a schematic showing "committed" and "possible" applications of graphite/PMR-15 composite materials on the PW1120 turbojet currently being developed by Pratt and Whitney Aircraft/Government Products Division (PWA/GPD). A committed applications is an application for which a metal back-up component is not being developed. The only committed applications for graphite/PMR-15 composites at this time are the external nozzle flaps and the airframe interface ring. PWA/GPD is in the process of completing its assessment of the various "possible" applications and anticipates that many of these will also become "committed", if engine test schedules can be met. The PW1120 engine is currently scheduled for production deliveries in 1986. Graphite/PMR-15 external nozzle flaps have been committed for production by PWA/GPD for its PW1130 turbofan engine. Production deliveries of the PW1130 are scheduled for 1984. Prepregs made from T300 or Celion 3000 uniweave fabrics and PMR-15 are being evaluated for fabrication of the nozzle flaps used on both the PW1120 and PW1130 engines.

The CASTS (Composites for Advanced Space Transportation Systems) pro- gram was undertaken by NASA Langley in 1975 to develop graphite/polyimide composites for application to future aerospace vehicles. As part of the CASTS Program, Boeing Aerospace Company developed manufacturing processes for fabrication of graphite/PMR-15 structural elements and demonstrated their structural integrity at temperature up to 316° C. 27 The structural elements consisted of flat panels, corrugated stiffeners, I-beams, hat stiffeners, honeycomb panels, and chopped fiber moldings. A section (76 cm wide x 203 cm long x 56 cm tapered to 15 cm thick) of a simulated shuttle orbiter aft body flap (full scale, 213 x

640 cm) was successfully fabricated. Thus, demonstrating that the manufacturing processes which were developed for structural elements could be adapted to large scale airframe hardware.

Figure 13 shows a mercury ion thruster for an auxiliary propulsion system being built by Hughes Space and Communications Group under contract to NASA Lewis. The ion propulsion system is scheduled for launch and testing on a future space shuttle flight. The thruster is equipped with a glass fabric/PMR-15 composite beam shield to protect the solar arrays and sensitive instrumentation on the spacecraft from ion-beam damage. The composite shield (approximate dimensions: 25 cm diameter x 20 cm length x 0.1 cm thickness) was selected over tantalum and titanium because of weight and structural considerations. The feasibility of using a glass fabric/PMR-15 composite shield was demonstrated by in-house fabrication and testing of full-scale beam shields.

CONCLUDING REMARKS

The in situ polymerization of monomer reactants (PMR) approach has been demonstrated to be a powderful approach for solving many of the processing difficulties associated with the use of high temperature resistant polymers as matrix resins in high performance composites. PMR-15, the PMR polyimide discovered in the early seventies, provides the best overall balance of processing characteristics and elevated temperature properties. The excellent properties and commercial availability of composites materials based on PMR-15 have led to their acceptance as viable engineering materials. PMR-15 composites are currently being used to produce a variety of high quality structural components. Increased use of these materials is anticipated in the future.

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TABLE L - MONOMERS USED FOR PMR-15 POLYIMIDE

STRUCTURE	NAME	ABBREVIATION
C-OMe	MONOMETHYL ESTER OF 5-NCRBORNENE- 2,3-DICARBOXYLIC ACID	NE
MeO-C C-OMe	DIMETHYL ESTER OF 3,3',4,4'- BENZOPHENONETETRACARBOXYLIC ACID	BTD€
H ₂ N-CH ₂ -NH ₂	4,4'-METHYLENEDIANILINE	MDA

CS-71803

TABLE II. - APPLICATIONS OF PMR-15 COMPOSITES

Component	Agency	Contractor	
Ultra-high tip speed fan blades QCSEE inner cowl F404 outer duct F101 DFE inner duct T700 swir1 frame JT8D reverser stang fairing	NASA-LeRC NASA-LeRC Navy/NASA-LeRC Air Force Army NASA-LeRC	PWA/TRW GE GE GE GE McDonnel-	
External nozzle flaps PW1120 PW1130 Shuttle orbiter aft body flap Ion thruster beam shield	Air Force NASA-LeRC NASA-LeRC	Douglas PWA ^a PWA Boeing Hughes	

^aCompany funded

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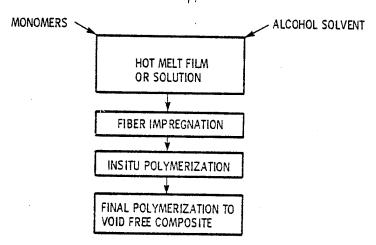


Figure 1. - Lewis PMR polyimide technology.

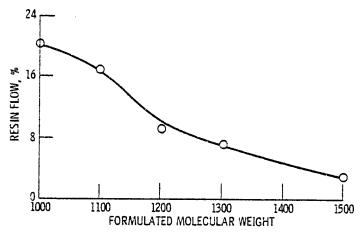


Figure 2. - Resin flow of HTS graphite/PMR composites (Resin flow is based on weight of resin flash formed during molding).

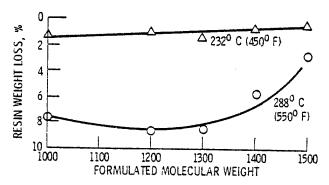


Figure 3. – Percent resin weight loss for PMR PI/HTS graphite fiber composites after 600-hr exposure in air at 232° C $(450^{\circ}$ F) and 288° C $(550^{\circ}$ F).

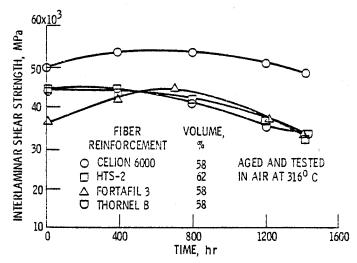


Figure 4. - Interlaminar shear strength of graphite fiber PMR-15 composites.

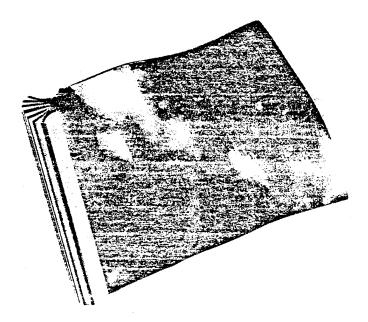


Figure 5. - Graphite fiber/PMR-15 polyimide fan blade (span, chord and maximum thickness = 28, 20, and 1.3 cm, respectively).

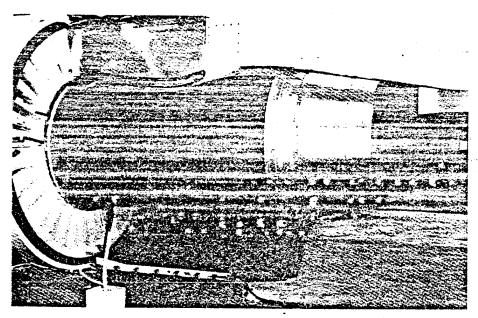


Figure 6. - Graphite fiber/PMR-15 polyimide inner eowl installed on QCSEE engine.

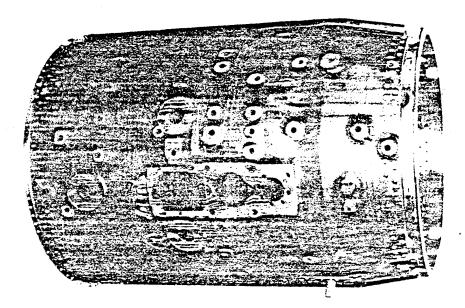


Figure 7. - Graphite fiber/PMR-15 outer duct after final machining.

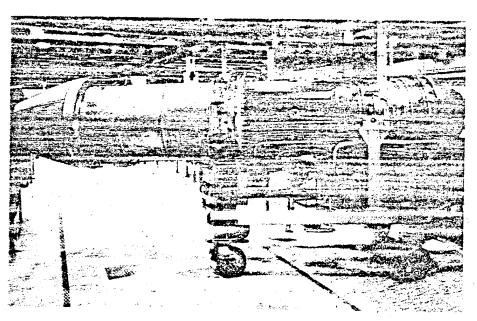


Figure 8. - Grapnite fiber/PMR-15 outer duct installed on an F404 engine (composite duct located directly above carriage).

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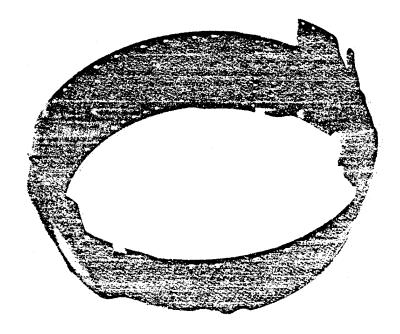


Figure 9. - Graphite fiber/PMR-15 F101 DFE inner duct (Diameter = 102 cm, length = 38 cm, and thickness = 9.15 cm.).

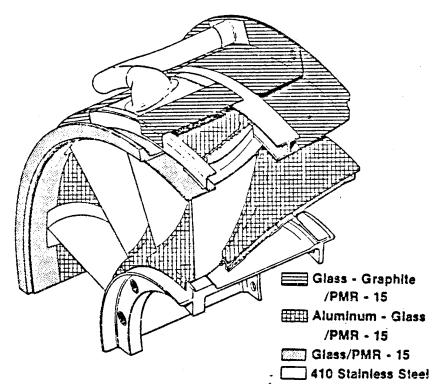


Figure 10. - Schematic section of the T700 PMR-15 composite swirl frame (0. D. \simeq 51 cm).

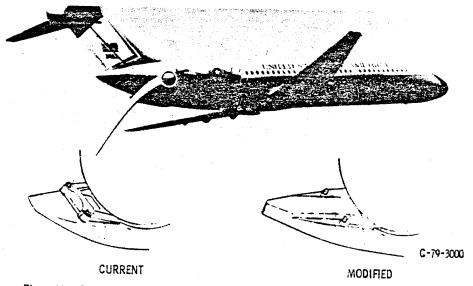


Figure 11. - Douglas DC-9 airplane. Inserts schematically show the current production metal fairing and the redesigned lower drag composite fairing made with Kelvar fabric/PMR-15.

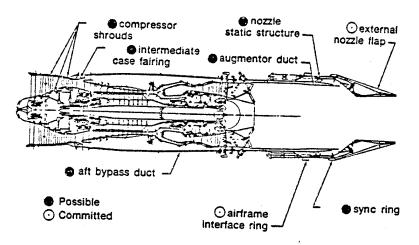


Figure 12. - Schematic of PW1120 showing applications of graphite/FMR-15 materials.

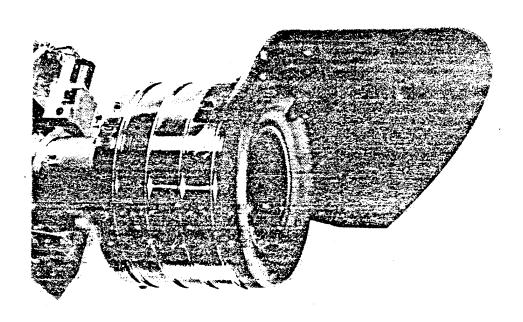


Figure 13. - Mercury ion thruster equipped with glass fabric/PMR-15 beam shield (shield diameter \pm 25 cm.